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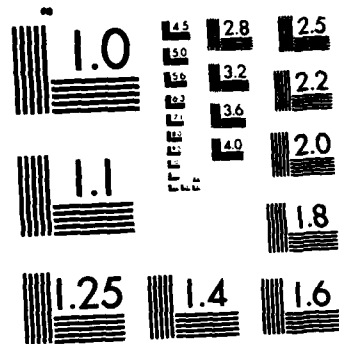
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Activation of Unimolecular Cyclobutene Isomerization

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Vibrational Energy Transfer at a Liquid Gallium Surface.

Activation of Unimolecular Cyclobutene Isomerization.

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ABSTRACT

Single collision vibrational energy transfer for a canonical ensemble ( $T=300K$ ) of cyclobutene molecules at a heated liquid gallium surface has been studied from 450K to 700K. Transport above the reaction threshold for isomerization to butadiene ( $E_0=32.4 \text{ kcal mole}^{-1}$ ) was used as the criterion for efficiency of vibrational energy accommodation. The efficiency was found to fall below strong collider behavior above 625K. Evidence of surface catalysis became important below 525K. The observed behavior is reminiscent of that found previously for other liquid (Sn) and solid (Au) metal surfaces.

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## INTRODUCTION

Conventional thermal energy transfer between gases and solids is an area that has undergone much experimental and theoretical scrutiny. Studies of translational and rotational energy transfer by molecules at well characterized surfaces and specific sites may be found in the literature(1-4). Recently, some attention has been given to energy transfer with somewhat ill-defined solid surfaces (polycrystalline materials in the low vacuum region). These studies have been concerned with the change in internal energy of an ensemble of molecules initially at a well defined (lower) temperature, after they have interacted with a solid surface of higher temperature. Reports of the magnitudes of vibrational accommodation coefficients have varied. Foner and Hudson(5) used a molecular beam technique to estimate  $\alpha_v=0.05$  for  $n\text{-C}_4\text{H}_{10}$  on a Pt filament at 1273K. Rosenblatt and coworkers(6) obtained translational and internal energy accommodation coefficients for a series of paraffins measured at relatively high pressures on a variety of polycrystalline surfaces. Their lower limit estimates for vibrational accommodation at room temperature on Fe were 0.36, 0.72, and 0.90 for  $\text{CH}_4$ ,  $n\text{-C}_4\text{H}_{10}$  and  $n\text{-C}_8\text{H}_{18}$  respectively. Amorebleta and Colussi, using a technique basically similar to that utilized in our laboratory found  $\alpha_v=0.47$ , 0.58 and 0.52, respectively, for  $n$ -butane,  $n$ -octane and 1-chlorobutane on silica surfaces at 350K (7). They also found that relaxation for these same compounds was more efficient on Pt (by a factor of 1.4-1.8 in  $\alpha_v$ ) and appeared to be quasi-independent of surface temperature between 350K and 700K.

Until recently, virtually no data existed for vibrational energy transfer at solid surfaces by polyatomic molecules at high levels of vibrational excitation. Such energy transfer studies conducted in this laboratory have

utilized the Variable Encounter Method (VEM) in which a controlled variable number of sequential collisions of gas molecules at some initial lower temperature is allowed to occur with a hot surface. The method has been fully described(8). The single collision ( $m=1$ ) version has been used to show a decrease of  $\alpha_v$  with temperature(9). In these systems, the criterion for collisional energy transfer is transport of reactant gas molecules above their reaction threshold. In our studies, done first on fused pyrex and quartz, the surfaces have usually been deliberately seasoned with the reactant (deactivation of "hot spots" and deposition of a mono- or multi-molecular layer) in order to reduce surface catalytic effects and to provide reproducible results(9,10). Deliberate seasoning of the surface with reactant has been a long-time common procedure in gas kinetic studies. Nonetheless, we have shown that such seasoning does not completely obscure effects due to the nature of the original underlying matrix(11). Work on cyclobutene isomerization to butadiene on these glass surfaces provided evidence for strong collider behavior at temperatures up to ~425K. A study by Yuan and Rabinovitch(11) showed strong collider behavior persisted up to 550K-600K for cyclobutene on variously treated, gold wire and plane surfaces; they found that preabsorbed  $O_2$  enhanced the efficiency of energy transfer. This concurred with reports by Somorjai and coworkers(12). Metals may behave as stronger colliders than pyrex and silica due to possible relaxation mechanisms that are unique to metals.

Energy accommodation between gases and liquids has received much less attention. The earliest work appears to be that of Alty and coworkers(13) who examined accommodation coefficients for several covalent liquids and their own vapors, as well as for Hg and its vapor. In all cases, except for water, penetration and absorption into the liquid rather than reflection was found.

Thomas and Petersen(14) looked at accommodation of He on a K-coated tungsten filament, just above and below the melting point of K, and found  $\alpha_v(338K) = 0.095$  and  $\alpha_v(328K) = 0.089$ . No discontinuity was observed at the melting point.

Very recently, Nilsson and Rabinovitch(15) reported on vibrational energy transfer between cyclobutene and liquid tin at temperatures up to 800K. Strong collider behavior was observed up to 550K. They found that the Sn surface, which most likely consisted of small islands of tin(II)oxide floating on liquid Sn(16), was strongly reminiscent of oxygen processed gold surfaces investigated by Yuan and Rabinovitch(11). They also observed no discontinuity in the vibrational accommodation coefficient at the melting point. Liquid tin is known to exhibit structure resembling that of solid  $\beta$ -tin.

The present study extends our work to a liquid gallium surface. The choice of suitable surfaces, in this case of metals, is limited greatly by the requirements of non-reactivity and low vapor pressures, for work at higher temperatures. Like Sn, Ga seems to be unreactive at the temperatures used here. It has the longest liquid range known of any metal. Its vapor pressure is reported to be  $10^{-6}$  torr at the highest temperature used in this study(17). Cyclobutene has a low reaction threshold ( $E_0 \sim 32 \text{ kcal mole}^{-1}$ ) for isomerization to 1,3-butadiene(18) and therefore is favorable for use as a subject molecule at moderate temperatures. Moreover, it is known to be relatively clean and uncomplicated as an experimental example of a thermal unimolecular reaction. At the reactant pressures used in the current study, this reaction is close to the low pressure fall off region so that virtually all molecules that are energized to levels above  $E_0$  decompose. Our previous



studies done on pyrex, silica, crystalline gold and liquid tin surfaces showed no catalytic behavior for cyclobutene isomerization. While some catalytic behavior is observed in the present system at the lower temperatures used, this does not negate the general import of the behavior observed at higher temperatures. The present technique affords a specific test of vibrational energy transfer at high energy levels (above  $E_0$ ), in contrast to conventional bulk energy accommodation studies.

## EXPERIMENTAL

Cyclobutene was synthesized according to the procedure of Fadel et. al.(19). GLC and GCMS analysis showed that it contained less than 0.05% 1,3-butadiene as an impurity. The sample was therefore used without further purification. The gallium (original purity > 99.9%) was further treated as follows: the metal was melted and liquid beneath the surface was drawn up into glass tubes and allowed to harden. The tubes were then cracked to yield clean rods of solid Ga.

The reaction chamber consisted of a 5 l pyrex bulb, the lower part of which was sealed to a 4 cm inner diameter flat bottom quartz well containing the liquid sample which was heated in a bath. The volume of Ga used was the minimum amount necessary to cover the bottom of the well. The liquid sample was not stirred; our previous experiments done on liquid Sn showed no difference in the observed rate of isomerization with rate of stirring(15). This greatly simplified the experimental design. The surface of the liquid Ga, while not a perfect mirror, was in general shiny, with slowly accumulating small grey patches of dross, especially at the perimeter edges of the surface; the surface was cleaned from time to time.

The quartz walls just above the level of the hot Ga (as well as the bulb itself) were maintained at or near room temperature. This was accomplished by wrapping the quartz well with 3/8" copper tubing and circulating cold water through it. At the highest temperature used (700K) the temperature of the walls never exceeded 325K. Molecules that leave the liquid surface accommodate with the cold bulb wall before restriking the hot surface.

A molten salt bath (53%  $\text{KNO}_3$ , 7%  $\text{NaNO}_3$ , 40%  $\text{NaNO}_2$ ) was used. The bath was contained in a stainless steel dish that had 4 cartridge heaters symmetrically encased within the bottom wall of the dish. The dish was wrapped in asbestos tape to minimize heat loss to the surrounding environment. For the majority of runs made in the temperature range 600-700K (excluding those at 629.5, 631.5 and 665.5K) an alternate heat source was also used. A two piece spherical heating mantle filled with sand replaced the cartridge heaters. The stainless steel dish was sunk in the sand up to its top edge. This allowed for uniform heating of the entire salt bath.

Temperature measurement was made by means of a 40 gauge chromel-alumel thermocouple probe that extended through the top of the pyrex bulb downward directly into the surface of the metal in the center of the well. Temperature measurements made on the molten salt bath showed the temperature fluctuation within the bath to be less than 5K.

In a typical run, the pyrex bulb was pumped down to  $\sim 10^{-6}$  torr prior to the introduction of the substrate. Sample pressures in the range  $2-6 \times 10^{-4}$  torr were employed. The duration of exposure of the cyclobutene sample to the hot Ga was varied in order to keep the percent reaction less than 15% and

usually below 5%. The reaction gas was then transferred for analysis. Products were analyzed by using a liquid support coated open tubular column at 0° C with He as the carrier gas. A flame ionization detection system was employed.

## RESULTS AND DISCUSSION

The reaction probability per collision  $P_c$  (i.e. the measure of transport of reactant molecules above the reaction threshold after a single collision with the hot surface) was calculated from the following expression,  $P_c = 4kV/\bar{S}\bar{c}$ ; where  $k$  is the apparent first order rate constant,  $V$  is the volume of the reaction vessel,  $S$  is the surface area of the liquid Ga, and  $\bar{c}$  is the average translational velocity of the reactant molecules which have equilibrated with the cold wall prior to collision with the hot surface.

Initially, a series of runs (Data set I) was made which established the general trend of the data for  $P_c$  vs.  $T$  for this system. These runs showed strong collider behavior above 525K but greater than strong collider at temperatures below this, suggesting a contribution from surface catalysis (this behavior has previously been observed and can be corrected (in whole or in part) by pretreatment (seasoning) of the surface(11)). As is well known, e.g. from very low pressure pyrolysis experiments(20), the importance of low activation energy surface catalysis/free radical contributions to the mechanisms of homogeneous gas-phase unimolecular reaction diminishes with increase of temperature. The second set of data (Data set II) was another investigation of the behavior of this system made after a lapse of time and with minor alterations to the apparatus and reactor. These experiments confirmed the results previously obtained. While showing the same trend in the variation of  $P_c$  with temperature, the second data set showed a small

systematic deviation from the first. This was taken to be indicative of a small discrepancy in the temperature measurement. The apparent temperature discrepancy is due to a difference in the presence and absence of a thin-wall glass tip at the end of the thermocouple in the two sets together with some difference in positioning of the thermocouple probe in the liquid Ga. Any repositioning of the thermocouple probe resulted in a small variation in the temperature measurement. In order to clean off any dross i.e. oxide (21) that had formed on the surface due to traces of oxygen, removal of the thermocouple probe was necessary. As this procedure was carried out between Data sets I and II, the above explanation seems the most likely cause of a systematic temperature variation. The relative temperature of the later runs was estimated to be low by  $\sim 7.5\text{K}$ .

Figure 1 is a plot of experimental results of  $P_c$  vs  $T$ . The solid curves show strong collider behavior ( $E_0 = 32.0\text{--}32.4 \text{ kcal mole}^{-1}$ ). Unlike the Sn studies which conform to simple strong collider behavior at low temperatures, the results here for runs made below  $\sim 525\text{K}$  show evidence for some catalysis. Defect from strong collider behavior was observed to occur above  $625\text{K}$ , analogous to the behavior with Sn. In general, and especially illustrated by Data set I, the results conform to strong collision behavior over the middle range. This concurs with studies of cyclobutene vibrational accommodation not only on liquid Sn, but also on seasoned gold and on  $\text{O}_2$ -processed gold surfaces(11).

Transport above the reaction threshold for isomerization of butadiene is used as the criterion for efficient vibrational energy accommodation. This is a more severe test than measurement of the average energy of the final

distribution as a whole, as in conventional accommodation coefficient measurements. In such cases, relatively large deviations from strong collider behavior for transitions at higher energy may not greatly alter the average energy of the distribution(22). The same behavior, however, can significantly alter the population above  $E_0$  and therefore lead to more sensitive determinations of the high energy collisional efficiency(9). The new population vector  $N^1$ , after a single collision is related to the population vector corresponding to the Boltzman distribution at the original gas temperature,  $N^0$ , by  $N^1 = PN^0$ , where  $P$  is the transition probability matrix. In this work, strong collider behavior was present below 625K. This corresponds to complete vibrational accommodation in a single collision.  $N^1$ , therefore, is simply the Boltzman distribution characteristic of the surface temperature. The value of the accommodation coefficient,  $\alpha_v$ , deduced above 625K depends on the form of  $P$  which is currently unknown. Studies in this laboratory have sought to ascertain the correct analytical form of  $P$  using both single- and multi-collision variations of the Variable Encounter Method(23-25).  $P$  can be partitioned at  $E_0$ ,

$$P = \begin{vmatrix} P_I & P_{III} \\ P_{II} & P_{IV} \end{vmatrix}$$

$P_I$  concerns transition probabilities between levels below  $E_0$ . These transitions contribute heavily to  $N^1$  and therefore to the average energy change  $\Delta E_{av}$ . Knowledge of  $P_I$  is most helpful for deducing values of  $\alpha_v$ . This information can be indirectly obtained by the Variable Encounter Method when  $m > 1$ .  $P_{II}$  contains transition probability elements from levels below  $E_0$  to those above and is probed by single collision studies.  $P_{III}$  is ascertained from detailed balance. The two variants ( $m = 1$ ,  $m > 1$ ) of the VEM technique can give complementary information about the correct analytical form of  $P$ (23,24).

The results of the present study concur with those of Nilsson and Rabinovitch(15), suggesting substantial accommodation on the surface and that the liquid Ga surface also behaves much like a solid metal surface with respect to energy transfer by polyatomic gas molecules. Interpretation of the structural properties of liquid Ga has led to the conclusion that a marked analogy exists between the short range order in liquid Ga and in the metastable monoclinic form  $\beta$ Ga(26), which usually forms when supercooled Ga crystallizes at low temperatures. The structure of liquid Ga has been studied by x-ray(27), neutron(28) and electron(29) diffraction. Early results suggested the presence of "psuedo" molecules of  $\text{Ga}_2$  with an interatomic distance of  $\sim 2.44\text{\AA}$  separated from each other by 2.7-3.3 $\text{\AA}$ ; this was explained as covalent short binding in liquid Ga similar to that found in orthorhombic  $\alpha$ Ga(30). More recent studies however(26,31) make the analogy with the less stable  $\beta$ Ga. Regardless of which hypothesis is valid the various studies agree that liquid Ga has some of the structural characteristics of a solid form.

Relatively long residence time of gas molecules and accommodation at the surface need not imply, and does not here mean that reaction takes place on the surface. Expressed otherwise, the strong collision behavior of Fig. 1 represents the prediction of the Boltzmann distribution and not the Tolman distribution. Our early results on seasoned silica surfaces with cyclopropane, where strong collider behavior was found at lower temperatures, first showed that ensuing reaction was characterized as low-pressure homogeneous gas phase behavior(8). The time scale for unimolecular reaction in Lindemann theory is here much longer than the residence time on the surface.

Is it possible that the "catalysis" noted earlier above at lower temperatures is not chemical in nature but represents highly extended lifetimes on the surface? Our earlier work on Au(11) and Sn(15) surfaces, as well as on silica surfaces(9), wherein the experimental curves did follow the strong collider curve at the same lower temperatures, indicates otherwise. The predicted magnitude of fractional surface coverage  $\theta$  in such case would be only  $\theta \sim 10^{-5}$ .

Finally the higher  $\alpha_v$  values found in this work on metal surfaces relative to studies in other laboratories (5,6,7) may be explained by the high temperature seasoning of the surface that occurs in our work.

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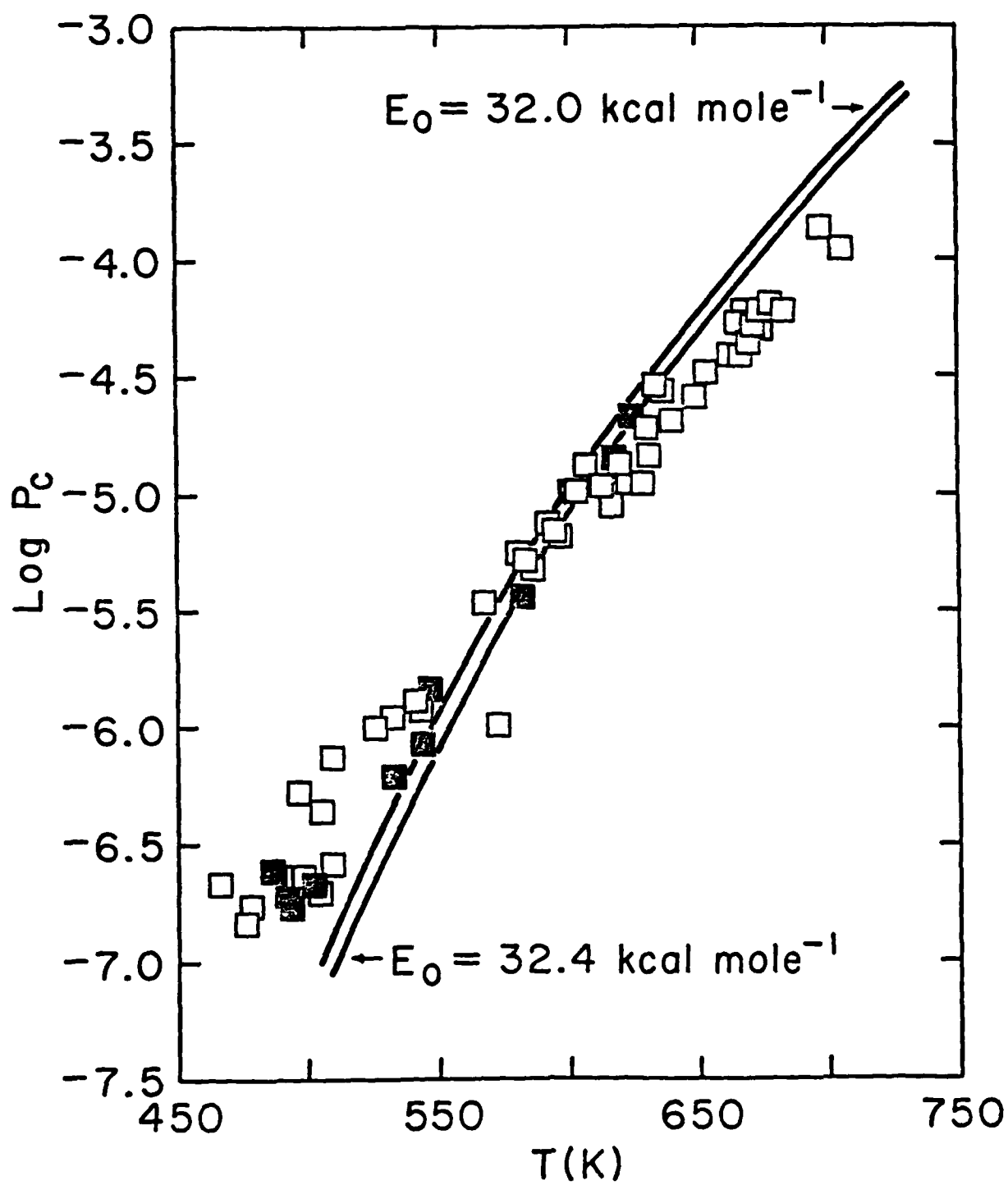
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Figure 1. Plot of experimental values of  $P_c$  vs  $T$ ; ■ and □ represent values from data sets I and II respectively (see text). Data set I, in particular, follow the strong collider curve fairly closely from 525-625K. The solid lines are strong collider curves ( $E_0 = 32.0$  and  $32.4$  kcal mole<sup>-1</sup>.)



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